ON THE REACTION OF DIALKYL ACYLPHOSPHONATE WITH 2-METHYLTHIAZOLIUM SALTS

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Dialkyl acylphosphonate worked as an acylating agent on the 2-methyl group of the 2-methylthiazolium and thiazolinium salts in the presence of the base, to give 2-acylidenethiazoline and thiazolidine derivatives respectively. Dialkyl [1-aryl (alkyl)-1-dialkylphosphatomethyl] phosphonate was also isolated as a by-product in the same reaction. For example, the reaction of 2,3-dimethylthiazolium iodide with diethyl benzoylphosphonate in the presence of 1,5-diazabicyclo[5,4,0]-5-undecene in the dimethylformamide suspension at -20°C gave 2-(3-methyl-2-thiazolinylidene)acetophenone in 73% yield and diethyl α-diethylphosphatobenzylphosphonate. Dialkyl acyl phosphonate afforded 2-acylidenethiazolines in better yield compared with acylchlorides and showed the apparent affinity to the carbanions.

Application of diethyl benzoylphosphonate to 1,2,3-trimethylbenzimidazolium iodide, however, formed a dimeric salt, 1,1',3,3'-tetramethyl-2,2'-(2-phenyltrimethylene)-bis(benzimidazolium)diiodide in addition to 2-(1,3-dimethyl-2-benzimidazolinylidene)acetophenone. On the basis of the difference of the reactivity between the 2-methylthiazolium and 2-methylimidazolium salts and the kinetic experiments, the mechanism of the acylating reaction was proposed.